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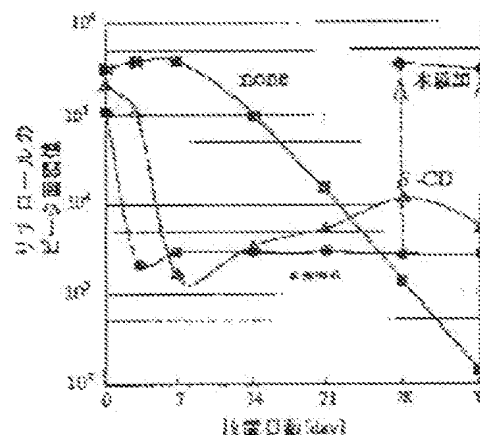
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(54) PERFUME-HOLDING POWDER AND COMPOSITION CONTAINING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a perfume-holding powder which is small in the temporal change of the perfume-releasing rate and can stably keep the perfume over a long period of time by allowing a mesoporous powder containing silicon oxide as a major component to hold the perfume.

SOLUTION: This perfume-holding powder is obtained by allowing a mesoporous powder, which consists of a mass-like powder containing silicon oxide as a major component and having pores of preferably 50-300 μm deep, forms sticks with an outside diameter of 20-200 μm and elongates the pores in the length direction of the stick, to hold a perfume. It is preferable that the above-stated mass-like powder is formed by initially dissolving a silicate salt with $\text{O}(\text{SiO}_2/\text{Y}_2\text{O}_3)<2$ (Y is an alkali metal atom) at pH 11 or more in the presence of 0.1-1.2 M concentration of a cationic surfactant, gradually adjusting the pH to 10.5 or less, forming a stick-like micell with the above-stated cationic surfactant, allowing to condense silicic acid on the above-stated stick-like micell and finally removing the cationic surfactant from the micell-like condensation product having the silicate salt formed by condensation as a shell.



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CLAIMS

[Claim(s)]

[Claim 1] Perfume maintenance fine particles characterized by making perfume hold to the meso porous fine particles which used oxidation silicon as the principal component.

[Claim 2] Perfume maintenance fine particles characterized by said meso porous fine particles being the massive fine particles which have a hole with a depth of 50-300nm in fine particles according to claim 1.

[Claim 3] Perfume maintenance fine particles characterized by the thing said whose meso porous fine particles are the outer diameters of 20-200nm, and which it is cylindrical and the hole is elongating in the die-length direction of a rod in fine particles according to claim 1.

[Claim 4] In fine particles according to claim 2 said meso porous fine particles The silicate (Y: alkali-metal atom) of $0 < \text{SiO}_2/\text{Y}_2\text{O}_3 < 2$ 0.1 - 1.2 M concentration, Dissolve by 11 or more pH under existence of a cationic surfactant, and pH is made or less into 10.5. Perfume maintenance fine particles which form a cylindrical micell with said cationic surfactant, and are made to carry out condensation of the silicic acid on this cylindrical micell, and are characterized by removing a cationic surfactant and being formed from the micell-like condensate which made the coat the silicate formed of said condensation.

[Claim 5] In fine particles according to claim 3 said meso porous fine particles The silicate (Y: alkali-metal atom) of $0 < \text{SiO}_2/\text{Y}_2\text{O}_3 < 2$ 0.3 - 1.2 M concentration, Dissolve by 11 or more pH under existence of a cationic surfactant, and pH is made or less into 10.5 within 30 minutes. Perfume maintenance fine particles which form a cylindrical micell with said cationic surfactant, and are made to carry out condensation of the silicic acid on this cylindrical micell, and are characterized by removing a cationic surfactant and being formed from the micell-like condensate which made the coat the silicate formed of said condensation.

[Claim 6] The constituent characterized by including perfume maintenance fine particles according to claim 1 to 5.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to amelioration of the perfume maintenance device which made support perfume maintenance fine particles and a constituent, especially meso porous fine particles.

[0002]

[Description of the Prior Art] Various matter, for example, perfume etc., is matter which vaporizes or is easy to deteriorate, and various kinds of approaches are taken from before over a long period of time [the] for stable maintenance. For example, it is inconvenient although the method of adjusting the vaporization rate of perfume by carrying out inclusion of the perfume molecule to the matter which has openings, such as a method of carrying out distributed maintenance of the perfume or a cyclodextrin, in resin etc. is mentioned, and the former is effective as an object for maintenance of the perfume for the interior of a room, and applied, for example to people. At this point, it is also possible to consider as the shape of fine particles thru/or a paste, for example, it can apply the latter perfume clathrates to the body etc.

[0003]

[Problem(s) to be Solved by the Invention] However, by the approach using said cyclodextrin etc., the technical problem that change of aroma reinforcement with time arose occurred. This invention is made in view of the technical problem of said conventional technique, the object has a small change of a perfume bleedoff rate with time, and it is in offering the constituent which moreover blended the perfume maintenance fine particles and it in which perfume stability maintenance is possible over long duration.

[0004]

[Means for Solving the Problem] In order to attain said object, when this invention person etc. inquired wholeheartedly, by making the silicate of specific silicon / alkali-metal ratio react under specific concentration, meso porous fine particles with the meso hole of the diameter of detailed, i.e., opening with a diameter of 2-50nm, were obtained, and it finds out that this can attain long-term maintenance of perfume, and fixed-ization of a bleedoff rate, and came to complete this invention. the perfume maintenance fine particles which start this invention in order to attain said object --- oxidation silicon --- a principal component --- carrying out --- abbreviation --- it is characterized by making perfume hold to the meso porous fine particles which have a uniform hole.

[0005] Moreover, in this invention, it is suitable that said meso porous fine particles are the massive fine particles which have a hole with a depth of 50-300nm. Moreover, in this invention, it is cylindrical and the thing said whose meso porous fine particles are the outer diameters of 20-200nm and which the hole is elongating in the die-length direction of a rod is suitable. In this invention said massive fine particles the silicate (Y: alkali-metal atom) of $0 < \text{SiO}_2/\text{Y}_2\text{O}_3 < 2$ Moreover, 0.1 - 1.2 M concentration, Dissolve by 11 or more pH under existence of a cationic surfactant, and pH is gradually made or less into 10.5. It is suitable to form a cylindrical micell with said cationic surfactant, and to remove a cationic surfactant and to be formed from the micell-like condensate which was made to carry out condensation of the silicic acid on this cylindrical micell, and made the coat the silicate formed of said condensation.

[0006] Moreover, the dissolution process in which said cylindrical fine particles dissolve the silicate (Y: alkali-metal atom) of $0 < \text{SiO}_2/\text{Y}_2\text{O}_3 < 2$ by 11 or more pH under existence of 0.3 - 1.2 M concentration and a cationic surfactant in this invention, It is suitable to make pH or less into 10.5 within 30 minutes, to form a cylindrical micell with said cationic surfactant, and to remove a cationic surfactant and to be formed from the micell-like condensate which was made to carry out condensation of the silicic acid on this cylindrical micell, and made the coat the silicate formed of said condensation. Moreover, the constituent concerning this invention is characterized by including said perfume maintenance fine particles.

[0007]

[Embodiment of the invention] this invention persons performed the following trials paying attention to the meso porous fine particles which used oxidation silicon as the principal component. That is, 0.5 mols (Na_2SiO_3) (0.5M) of specific metasilicate and behenyl trimethylammonium chloride (BTC) 0.1mol (0.1M) were dissolved in 1l. ion exchange water. Temperature at this time was made into 70 degrees C, added 2N-hydrochloric acid by the rate of flow of 120 ml/min immediately after the dissolution, and adjusted pH to 8-9. Then, filtration and rinsing were performed, it calcinated at 700 degrees C for 3 hours, and cylindrical meso porous fine particles were obtained.

[0008] The supporter of linalool (perfume) was formed using these cylindrical meso porous fine particles and beta-cyclodextrin (beta-CD). These supporters were left in 40-degree-C thermostat, and the linalool concentration of the head space section was measured by GC-MAS. A result is shown in drawing 1. In addition, the peak area value showed linalool concentration.

[0009] In the case of a linalool simple substance, it decreases quickly with progress of neglect days so that more clearly than this drawing. On the other hand, when beta-CD is used as support, it becomes the minimum in about one week after neglect, and goes up gradually until after about one month after that, and if time amount passes further, concentration will decrease. This change is only considered that decomposition thru/or denaturation of beta-CD has also influenced rather than fluctuation of the vaporization rate of perfume. On the other hand, when the cylindrical meso porous fine particles concerning this invention are used as support, a steady state will be reached in about three days, and a subsequent concentration change will hardly be produced.

[0010] What should furthermore be observed is that the perfume concentration in a head space rises rapidly, i.e., a vaporization rate changes, when water is added to the perfume maintenance fine particles concerning this invention. Although there is also a point unknown about this cause if it has the uniform diameter of opening and perfume is held in it, the meso hole of meso porous fine particles used by this invention. While a vaporization rate becomes fixed almost in accordance with meso hole opening area irrespective of the change in perfume, when water is poured in, since the touch area of perfume and the open air has the comparatively high hydrophilic property inside a meso hole, perfume and water permute it, and it is considered because perfume is extruded by the meso hole exterior. In addition, it is obtained as a result of especially the meso porous fine particles used suitably examining behavior of water-soluble materials at the time of dissolving silicic acid with alkali in this invention. .

[0011] And when this invention persons advanced examination, to obtain homogeneous high meso porous fine particles extremely was shown clearly by being referred to as $0 < \text{SiO}_2/\text{Na}_2\text{O} < 2$, and carrying out condensation of the silicate ion in a dissolution condition on a quarternary-ammonium-salt micell. If said $\text{SiO}_2/\text{Y}_2\text{O}$ exceed 2, the homogeneity of the meso hole of the fine particles obtained eventually falls and is not desirable. At this point, when $\text{SiO}_2/\text{Y}_2\text{O}$ generally uses the water glass exceeding 2 etc. as a raw material, if a cationic surfactant is made to live together, it can become cloudy, and a dissolution condition cannot be maintained, and homogeneous meso porous fine particles cannot be obtained. Thus, although there are some which are shown in Patent Publication Heisei 5-503499 as a technique in which $\text{SiO}_2/\text{Y}_2\text{O}$ forms meso porous fine particles from two or more presentations, it is the technique of preparing the meso porous fine particles of aluminium compound coexistence substantially, and this has a possibility that perfume may denaturalize by the catalytic activity by the aluminium compound, and is not desirable. Although the meso porous fine particles of the shape of massive thru/or a rod can be prepared because silicate concentration is in the specific range, a rod-like structure is [among these] in addition, desirable especially in respect of perfume maintenance capacity then.

[0012] Hereafter, the suitable operation gestalt of this invention is explained.

The silicate at the time of manufacturing the meso porous fine particles used in silicate this invention is $0 < \text{SiO}_2/\text{Y}_2\text{O} < 2$. (Y: alkali-metal atom) It is a thing and Na or K is suitable in respect of the ease of receiving etc. especially as said alkali-metal atom. Said silicate can be formed by making various kinds of "matter containing silicon" react with alkali, such as NaOH. As the above "the matter containing silicon", silicon oxide, silicate, a silicon alkoxide, water glass, etc. are mentioned. As silicate, Na_2SiO_3 , Na_4SiO_4 grade, etc. are mentioned.

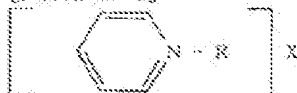
[0013] Moreover, as a silicon alkoxide, although tetramethyl alt.silicate, tetraethyl alt.silicate, etc. are mentioned, since it is low, being used with silicate is suitable for reactivity independent [these]. . Moreover, as water glass, JIS No. 1, JIS No. 2, JIS No. 3, etc. are mentioned, for example. In addition, these "matter containing silicon" is difficult for the most to be unable to maintain a dissolution condition but

to form homogeneous meso porous fine particles, if the cationic surface active agent which $\text{SiO}_2/\text{Na}_2\text{O}$ is over 2.0, and mentioned later exists. It is required by adding alkali chemicals, such as a sodium hydroxide, and dissolving there to obtain the silicate which may be displayed as $0 < \text{SiO}_2/\text{Y}_2\text{O} < 2$.

[0014] In addition, although the silicate used in this invention does not have trouble in the formation of meso porous fine particles itself, in the case of $\text{SiO}_2/\text{Na}_2\text{O} < 0.5$, its alkali chemicals are superfluous, and it produces futility in it. Moreover, in $2 < \text{SiO}_2/\text{Na}_2\text{O}$, the water solution cannot be in a perfect dissolution condition easily in the state of nebula, and becomes difficult [the formation of homogeneous meso porous fine particles itself]. for this reason, this invention -- setting -- $0 < \text{SiO}_2/\text{Y}_2\text{O} < 2 < 0.5 < \text{SiO}_2/\text{Y}_2\text{O} < 1.9$ are especially preferably desirable.

[0015] As cationic surface-active-agent one side and a cationic surface active agent, quarternary ammonium salt is desirable. As this quarternary ammonium salt, they are alkyl system quarternary-ammonium-salt [R₄N] X and ring type quarternary ammonium salt [0016].

[Formula 1]



In addition, in each above-mentioned ammonium salt, what has structures, such as R: H, an alkyl group, an allyl group, benzyl, a phenyl group, a hydroxyl group, hydroxy alkoxyl group X: Cl⁻, Br⁻, I⁻, and NO₃⁻, is illustrated.

[0017] These quarternary ammonium salt needs to form a micell by making pH or less into 10.5 in a water solution. In addition, R of said quarternary ammonium salt tends to form the shape especially of a rod as it is an alkyl group exceeding a carbon number 18. Moreover, when R of quarternary ammonium salt uses a with a carbon number of 18 or less alkyl group, become easy to suppose that it is cylindrical by doing 0.1-3M coexistence of salts (NaCl etc.) with acid residue other than silicic acid, for example, Cl⁻, Br⁻, and I⁻. Moreover, in this invention, the characteristic manufacture approach of meso porous fine particles is constituted like as follows.

[0018] A cationic surfactant is mixed with the dissolution process aforementioned silicate, and it is made to go up to the temperature which a room temperature thru/or both dissolve. When pH at the time of mixing is 11 or less, in the case of $\text{SiO}_2/\text{Na}_2\text{O} > 2$, alkali chemicals are added, and it is referred to as 11 or more pH and $\text{SiO}_2/\text{Na}_2\text{O} < 2$. extent which temperature up will take if both dissolve the holding time which this reaction takes -- it is comparatively good in a short time.

[0019] in addition, the rate of a cationic surfactant to silicate -- a mole ratio -- desirable -- 0.02-1.0 -- it is 0.05-0.3 especially preferably. When the cationic surface active agent of the amount of the cylindrical micell of said cationic surface active agent of generation decreases in the case of less than 0.02 in a mole ratio to silicate and a mole ratio exceeds 1.0, an unreacted cationic surface active agent remains in a large quantity, and becomes useless.

[0020] To the solution obtained at the condensation process above-mentioned dissolution process, an acid is added and pH is made or less into 10.5. Consequently, a cationic surfactant thru/or its spherical micells gather, and a cylindrical micell is formed. Moreover, by 11 or more pH, it condenses because the silicate ion which suited the dissolution condition sets to 10.5 or less pH, and silicic acid is arranged at the periphery of the cylindrical micell of said cationic surfactant.

[0021] The dispersion liquid which the clearance process above-mentioned fine particles condensed are filtered, and a cationic surfactant is removed after that. Rinsing and baking are mentioned as this clearance actuation. A cationic surfactant is removed by this clearance actuation and meso porous fine particles can be obtained.

[0022] In examination **** of $\text{SiO}_2/\text{Y}_2\text{O}$, and this invention, characteristic $\text{SiO}_2/\text{Y}_2\text{O}$ were examined. That is, the sodium-hydroxide (Nakarai Tesuku make) optimum dose of a special grade chemical is dissolved in 1l. of ion exchange water, and 300g (# made from Aerosil 200) of silicon dioxides of a commercial item is added and agitated. These dispersion liquid were calcinated at 700 degrees C for 5 hours, and the specific silicate was obtained. And this invention persons prepared the specific silicate of various $\text{SiO}_2/\text{Na}_2\text{O}$ as shown in a table 1, and tried manufacture of meso porous fine particles by making it into a raw material.

[0023]

[A table 1]

	$\text{SiO}_2/\text{Na}_2\text{O}$ 0.5	1.0	1.5	2.0	pH 12.05	11.95	11.65	11.35
Dissolution condition	The full dissolution	full dissolution	Full dissolution	Translucent	Specific surface area			

1066 1126 1142 1052----- [0024] In addition, it carried out by doubling measurement of an X diffraction, this measurement -- the JEOL make -- it carried out by part for 2 times (2theta)/by making CuK alpha rays into X line source using JDX-350. Slit width is -0.2mm [per degree] - 1 time. From this experimental result, if a specific silicate is in a dissolution condition, hexagonal structure is formed from the result of an X diffraction. However, in the condition that a specific silicate does not dissolve thoroughly, the meso porous fine particles which hexagonal structure may not be formed and have a homogeneous meso hole are not obtained.

[0025] As for $\text{SiO}_2/\text{Na}_2\text{O}$, less than 2.0 are desirable, and it is understood in having used 2.0 or more things, such as water glass, as they were at this point that proper meso porous fine particles cannot be manufactured so that more clearly than the above-mentioned table. And in order to have formed hexagonal structure in stability and to have considered as the homogeneous meso hole, especially about 1.9 were suitable for $\text{SiO}_2/\text{Na}_2\text{O}$.

[0026] In order to homogenize meso porous fine particles in silicate concentration this invention, it is suitable to adjust silicate concentration. That is, a specific metasilicate predetermined mol and a behenyl trimethylammonium chloride (BTC) predetermined mol were dissolved in 1L ion exchange water. Temperature at this time was made into 70 degrees C, added the 2-N hydrochloric-acid water solution at the rate of 120 ml/min immediately after the dissolution, and adjusted pH to 8-9. Then, filtration and rinsing were performed, it calcinated at 700 degrees C for 3 hours, and powder was obtained.

[0027]

[A table 2]

----- Meta-silicic acid concentration (M) 0.15 0.5 1.0 1.5 BTC (M)
0.03 0.1 0.2 0.3 ----- Description Massive Cylindrical meso porous
Cylindrical meso porous Cylindrical non porous Drawing 2 Drawing 3 Drawing 4 Drawing 5 -----

[0028] Silicic acid concentration serves as massive meso porous fine particles in 0.15M so that more clearly than this result. Moreover, in 1.5M, although it is cylindrical, opening is almost lost. And it was checked that are easy to become meso porous fine particles with silicate concentration massive 0.1-0.5M, and it is easy to become cylindrical meso porous fine particles by 0.3-1.2M by examination of this invention persons. In addition, in 0.3-0.5M, both mixture was checked and the abundance-ratio was changed according to other conditions mentioned later.

[0029] In order to form meso porous fine particles in this invention, it is suitable for silicic acid concentration that it is 0.1-1.2M, and in order to consider as cylindrical meso porous fine particles further, it is more suitable for it than the above result that it is 0.3-1.2M.

[0030] In order to form fine particles in meso porous in acid addition rate this invention for pH adjustment, it is suitable to adjust the addition rate of the acid for pH adjustment added in said condensation process. That is, 0.5 mols of specific metasilicate and 0.1 mols (BTC) of behenyl trimethylammonium chloride were dissolved in 1L ion exchange water like the above (pH11.5). Temperature at this time was made into 70 degrees C, and adjusted pH to 9 in the 2-N hydrochloric-acid water solution immediately after the dissolution. The addition rate of 2N-hydrochloric acid at this time was changed. Then, filtration and rinsing were performed, it calcinated at 700 degrees C for 3 hours, and powder was obtained.

[0031]

[A table 3]

----- A hydrochloric-acid addition rate 2 ml/min Time amount which
120 ml/min pH change takes 150 minutes 2.5 minutes -----
Description Massive meso porous Cylindrical meso porous Drawing 6 Drawing 3 -----

[0032] 2N-hydrochloric-acid addition rate serves as cylindrical meso porous fine particles by 120 ml/min with massive meso porous in 2 ml/min so that more clearly than this result. In order to obtain desirable cylindrical meso porous fine particles especially in this invention as a result of a still more detailed examination, it is suitable for the hydrochloric-acid addition rate in said conditions that they are 10 ml/min (less than [pH business time amount 30 minute]).

[0033] In order to form fine particles in the shape of [suitable] a rod especially in acid concentration this invention for pH adjustment, it is suitable to adjust acid concentration for pH adjustment added in said condensation process. That is, 0.5 mols of specific metasilicate and 0.1 mols (BTC) of behenyl trimethylammonium chloride were dissolved in 1L ion exchange water like the above (pH11.5). Temperature at this time was made into 70 degrees C, and adjusted pH for the hydrochloric-acid water solution of various concentration to 9 in 120 ml/min immediately after the dissolution. Then, filtration and rinsing were

performed like the above, it calcinated at 700 degrees C for 3 hours, and powder was obtained.

[0034]

[A table 4]

----- A hydrochloric-acid addition rate 0.2Ns 2Ns 5Ns Time amount
 which pH change takes 35 minutes 2.5 minutes 1 minute -----
 Description Massive meso porous Cylindrical meso porous Cylindrical meso porous Drawing 7 Drawing 3
 Drawing 8 ----- [0035] If 0.2N-hydrochloric acid is used so that more
 clearly than this result, it will become massive meso porous, and it becomes being more than 2N-
 hydrochloric acid with cylindrical meso porous fine particles. And when it sees by the time amount which pH
 adjustment takes, too, if it has been 30 minutes or more, it will become massive, and there is an inclination
 which becomes cylindrical in 30 or less minutes. And especially as perfume maintenance fine particles of this
 invention, when cylindrical meso porous fine particles are used, it is desirable to demonstrate the
 outstanding perfume maintenance effectiveness and to consider as cylindrical meso porous fine particles at
 this point.

[0036] Next, deodorant powder as shown in the following table 5 was prepared, and the effectiveness of the
 perfume maintenance fine particles concerning this invention was verified. It prepared so that perfume
 concentration might become with 1% among a constituent in any case.

[A table 5]

----- Example 1 of a trial Example 2 of a trial Example 3 of a trial
 The example 4 of a trial ----- Scent Charge Perfume maintenance fine
 particles 5.0 Perfume maintenance silica gel 5.0 Perfume maintenance cyclodextrin 5.0 Perfume simple
 substance 1.0 ----- Usually, fine particles Aluminum chloro hydrate
 5.0 5.0 5.0 5.0 Zinc oxide 5.0 5.0 5.0 5.0 talc 80.0 80.0 80.0 84.0 -----
 --- Oil content Liquid paraffin 5.0 5.0 5.0 5.0 ----- Effectiveness The
 scent of a product (three days after) + ++ +++++ Scent of a product (one month after) + + ++ + Scent (one
 month after) +++ at the time of an activity + ++ +----- [0037] In
 addition, in manufacture of each example of a trial, after teaching powder to the Henschel mixer,
 respectively and agitating to homogeneity, the remaining components were added and it mixed to
 homogeneity. The atomizer ground mixture, compression molding was carried out at the container, and
 deodorant powder was obtained. Moreover, preservation was performed under room temperature
 disconnection.

[0038] According to the deodorant powder using the perfume maintenance fine particles concerning this
 invention, the scent of a product maintains a fine scent condition so strongly so that more clearly than the
 above result, but at the time of an activity, it permutes by the sweat on the skin thru/or sebum, and quite
 strong aroma is demonstrated. According to the deodorant powder furthermore applied to this invention,
 the absorption of sebum occurs and the stickiness after an activity was controlled good.

[0039] Next, this invention person etc. considered the meso porous fine particles, the ratio, and the relation
 of effectiveness of perfume.

[A table 6]

----- The example of combination 5 6 6 7 8 9 10 11 12 -----
 ----- meso porous fine particles 0.01 0.1 0.5 1.0 5.0 10.0 30.0 50.0 80.0 Perfume
 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 ----- usually, fine particles
 Aluminum chloro hydrate 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5.0 Zinc oxide 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5.0
 Talc Remainder Remainder Remainder Remainder remainder Remainder Remainder Remainder -----
 ----- Oil content Liquid paraffin 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5.0 -----
 ----- Scent Immediately after manufacture + + ++ ++ + + + + + One
 month after + + + + + + + + At the time of an activity ++ ++ +++ +++ +++ +++ +++ ++ +-----

[0040] To the perfume 1 weight section, although fine-particles-izing is fully
 possible in meso porous fine particles being the 0.01 - 0.1 weight section, the perfume vaporization under
 preservation tends [a little] to advance, and although the scent at the time of an activity is the practical
 use range, it becomes a little weak, so that more clearly than the above-mentioned table 6. Moreover, also
 when meso porous fine particles exceed 30 weight sections, probably because whenever [opening / of meso
 porous fine particles] becomes high too much, it is in the inclination for a scent to become weak a little.
 Therefore, as for the mixing ratio of perfume and meso porous fine particles, about 1:0.5-1:30 is desirable at
 a weight ratio. In addition, the meso porous fine particles used in this invention have the messy makeup

prevention effectiveness by having the outstanding oil absorption nature and absorptivity.

[0041] In this invention, in order to manufacture perfume maintenance fine particles, it is good for the meso porous fine particles obtained as mentioned above only by kneading liquefied perfume thru/or the perfume which liquefied. Moreover, according to the system with which the class or perfume maintenance fine particles of the matter is blended, it is also suitable in the front face of meso porous fine particles hydrophobing and to carry out hydrophilization processing.

[0042]

[Example] Hereafter, the more concrete example of this invention is explained.

Example 1 400g (Nakarai Tesuku make) of sodium hydroxides of the manufacture special grade chemical of massive meso porous fine particles is dissolved in 1L of ion exchange water, and 300g (# made from Aerosil 200) of silicon dioxides of a commercial item is added and agitated. These dispersion liquid were calcinated at 700 degrees C for 5 hours, and the specific silicate (NaSiO_3) was obtained. 0.5 mols of said specific silicates and stearyl trimethylammonium chloride 0.1mol were added to 1L of ion exchange water, and it dissolved at 50 degrees C. pH at this time was 11.8. Furthermore, 2N-HCl was ****(ed) and pH was adjusted to 8.5. Then, filtration and rinsing were repeated 5 times, and acetone washing was carried out and it dried. This desiccation powder was calcinated at 700 degrees C for 5 hours, and massive meso porous fine particles were obtained.

[0043] Example 2 0.5 mols (Nakarai Tesuku) of anhydrous specific metasilicate of manufacture marketing of massive meso porous fine particles and stearyl trimethylammonium chloride 0.1mol were added to 1L of ion exchange water, and it dissolved at 70 degrees C. pH at this time was 11.75. Furthermore, 2-N HCl was ****(ed) and pH was adjusted to 8.5. Then, filtration and rinsing are repeated 5 times, and acetone washing was carried out and it was made to dry. This desiccation powder was calcinated at 700 degrees C for 5 hours, and massive meso porous fine particles were obtained. The TEM photograph of the massive meso porous fine particles obtained as mentioned above is shown in drawing 9. When opening prolonged in parallel was shown in this drawing in fine particles and having been observed similarly, in this invention, the opening depth was 50-300nm.

[0044] Example 3 30g (Nakarai Tesuku make) of sodium hydroxides of the manufacture special grade chemical of massive meso porous fine particles is dissolved in 1L of ion exchange water, and 30g (# made from Aerosil 200) of silicon dioxides of a commercial item is added and agitated. Stearyl trimethylammonium chloride 0.1mol was added to this solution, and it dissolved in it at 70 degrees C. pH at this time was 11.5. Furthermore, 2N-HCl was ****(ed) and pH was adjusted to 8.5. Then, filtration and rinsing were repeated 5 times, and acetone washing was carried out and it dried. This desiccation powder was calcinated at 700 degrees C for 5 hours, and massive meso porous fine particles were obtained. Nitrogen adsorption isotherm is shown in drawing 11, and the diameter distribution of opening is shown for X diffraction drawing of the meso porous fine particles obtained here in drawing 10 at drawing 12, respectively.

[0045] From drawing 10, diffraction reinforcement shows four diffraction peaks which show hexagonal structure structure. Moreover, the steep standup of the relative vapor pressure (P/p_0) =0.35 neighborhood of the nitrogen adsorption isotherm shown in drawing 11 is as the diameter distribution of opening which shows the homogeneity of the diameter of opening and is more specifically shown in drawing 12.

[0046] Next, X diffraction drawing of meso porous fine particles which manufactured similarly is shown in drawing 13 except having transposed said sodium hydroxide to the potassium hydroxide by equimolar. From this drawing, even if it is alkali other than a sodium hydroxide, it is understood that it can use for manufacture of the meso porous fine particles of this invention.

[0047] Example 4 0.5 mols (Nakarai Tesuku) of anhydrous specific metasilicate of manufacture marketing of massive meso porous fine particles and cetyl trimethylammonium chloride 0.1mol were added to 1L of ion exchange water, and it dissolved at 70 degrees C. pH at this time was 11.84. Furthermore, 2-N HCl was ****(ed) and pH was adjusted to 8.5. Then, filtration and rinsing were repeated 5 times, and acetone washing was carried out and it dried. This desiccation powder was calcinated at 700 degrees C for 5 hours, and massive meso porous fine particles were obtained.

[0048] Example 5 0.5 mols (Nakarai Tesuku) of anhydrous specific metasilicate of manufacture marketing of massive meso porous fine particles and lauryl trimethylammonium chloride 0.5mol were added to 1L of ion exchange water, and it dissolved at 70 degrees C. pH at this time was 11.92. Furthermore, 2-N HCl was ****(ed) and pH was adjusted to 8.5. Then, filtration and rinsing were repeated 5 times, and acetone washing was carried out and it dried. This desiccation powder was calcinated at 700 degrees C for 5 hours, and massive meso porous fine particles were obtained.

[0049] Example 6 Orthosilicic acid sodium (Nakarai Tesuku) 0.5mol of manufacture marketing of massive meso porous fine particles, stearyl trimethylammonium chloride 0.1mol, and phenyltrimethylammonium chloride 0.1mol were added to 1l. of ion exchange water, and it dissolved at 70 degrees C. pH at this time was 12.05. Furthermore, 2-N HCl was ****(ed) and pH was adjusted to 8.5. Then, filtration and rinsing were repeated 5 times, and acetone washing was carried out and it dried. This desiccation powder was calcinated at 700 degrees C for 5 hours, and massive meso porous fine particles were obtained.

[0050] Example 7 Stearyl trimethylammonium chloride 0.5mol was added into the mixed liquor of 500g (SiO₂/Na₂O=2.0) of water glass of manufacture marketing of massive meso porous fine particles, and 500g of ion exchange water, and it dissolved in it at 70 degrees C. pH at this time was 11.68. Furthermore, 2-N HCl was ****(ed) and pH was adjusted to 8.5. Then, filtration and rinsing were repeated 5 times, and acetone washing was carried out and it dried. This desiccation powder was calcinated at 700 degrees C for 5 hours, and massive meso porous fine particles were obtained.

[0051] Example 8 Distributed and dissolved manufacture SiO₂30g of massive meso porous fine particles, and stearyl trimethylammonium chloride 0.1mol at 1l. of ion exchange water, and add 2g NaOH, and it was made to dissolve, and agitated at 70 degrees C for 3 hours. pH at this time was 11.23. Furthermore, 2-N HCl was ****(ed) and pH was adjusted to 8.5. Then, filtration and rinsing were repeated 5 times, and acetone washing was carried out and it dried. This desiccation powder was calcinated at 700 degrees C for 5 hours, and massive meso porous fine particles were obtained.

[0052] The physical properties of the meso porous fine particles manufactured according to each above example are shown in the following table 7.

[A table 7]

	d100 (A)	a0 (A)	S.S.A (m ² /g)	TotalPoreVolume (cc)
An example 1	36.78	42.47	1125	2.06
examples 2	38.38	44.32	1074	1.73
examples 3	35.31	40.77	1210	1.84
examples 4	34.62	39.98	1165	1.01
examples 5	33.31	38.46	637	0.51
example 6	36.78	42.47	1077	2.32
examples 7	37.56	43.37	1220	1.22
example 8	36.03	41.61	1242	1.01

[0053] Example 9 0.5 mols (Na₂SiO₃) of manufacture specific metasilicate of cylindrical meso porous fine particles and behenyl trimethylammonium chloride (BTC) 0.1mol were dissolved in 1l. ion exchange water. Temperature at this time was made into 70 degrees C, added 2N-hydrochloric acid by the rate of flow of 120 ml/min immediately after the dissolution, and adjusted pH to 8-9. Then, filtration and rinsing were performed, it calcinated at 700 degrees C for 3 hours, and powder was obtained. Nitrogen adsorption isotherm is shown in drawing 15, and the diameter distribution of opening is shown for X diffraction drawing of the cylindrical meso porous fine particles obtained here in drawing 14 at drawing 16, respectively.

[0054] From drawing 14, diffraction reinforcement shows four diffraction peaks which show hexagonal structure. Moreover, the steep standup of the relative vapor pressure (P/p₀) =0.45 neighborhood of the shown nitrogen adsorption isotherm is as the diameter distribution of opening which shows the homogeneity of the diameter of opening and is more specifically shown in drawing 16 drawing 15. And the comparison at the time of performing preparation of mass and cylindrical meso porous fine particles by the same approach is shown.

[0055]

[A table 8]

	Massive meso porous fine particles	Cylindrical meso porous fine particles
Na ₂ SiO ₃	0.5 mol/l	0.5 mol/l
specific surface area	1100m ² /g	900m ² /g
oil absorption	300ml / 100g	500ml / 100g
pole diameter	30A	35A

Cylindrical meso porous fine particles have large oil absorption, although specific surface area is smaller than massive meso porous fine particles, and also doubling and having the outstanding oil absorption property is understood so that more clearly than the above-mentioned table 8.

[0056] Example 10 0.5-1.2 mols (Na₂SiO₃) of manufacture specific metasilicate of cylindrical meso porous fine particles and 0.05-0.24 mols (BTC) of behenyl trimethylammonium chloride are dissolved in 1l. ion exchange water. Temperature at this time was made into 70 degrees C, and adjusted pH to 8-9 with 2N-hydrochloric acid immediately after the dissolution. Then, filtration and rinsing were performed, it calcinated at 700 degrees C for 3 hours, and cylindrical meso porous fine particles were obtained. In addition, it was referred to as Na₂SiO₃/BTC=1/0.1 thru/or 1/0.2. Within the limits of this, each was able to prepare cylindrical meso porous fine particles.

[0057] Example 11 0.5-1.2 mols (Na₂SiO₃) of manufacture specific metasilicate, 0.05-0.24 mols (STC) of

stearyl trimethylammonium chloride, and 0.5-2 mols (NaCl) of sodium chlorides of cylindrical meso porous fine particles are dissolved in 1l. ion exchange water. Henceforth, cylindrical meso porous fine particles were obtained like said example 10. In addition, it was referred to as $\text{Na}_2\text{SiO}_3/\text{STC}/\text{NaCl}=1/0.1/1-4$ thru/or $1/0.2/1-2$. Within the limits of this, each was able to prepare cylindrical meso porous fine particles.

[0058] Example 12 0.5-1.2 mols (Na_2SiO_3) of manufacture specific metasilicate, 0.05-0.24 mols (STC) of stearyl trimethylammonium chloride, and 0.5-2 mols (NaBr) of sodium bromides of cylindrical meso porous fine particles are dissolved in 1l. ion exchange water. Henceforth, cylindrical meso porous fine particles were obtained like said example 10. In addition, it was referred to as $\text{Na}_2\text{SiO}_3/\text{STC}/\text{NaBr}=1/0.1/1-4$ thru/or $1/0.2/1-2$. Within the limits of this, each was able to prepare cylindrical meso porous fine particles.

[0059] Example 13 0.5-1.2 mols (Na_4SiO_4) of manufacture orthosilicic acid sodium of cylindrical meso porous fine particles and 0.05-0.24 mols (BTC) of behenyl trimethylammonium chloride are dissolved in 1l. ion exchange water. Henceforth, cylindrical meso porous fine particles were obtained like said example 10. In addition, it was referred to as $\text{Na}_4\text{SiO}_4/\text{BTC}=1 / 0.1 - 1/0.2$. Within the limits of this, each was able to prepare cylindrical meso porous fine particles.

[0060] Example 14 0.5-1.2 mols (Na_2SiO_3) of manufacture specific metasilicate, 0.05-0.24 mols (BTC) of behenyl trimethylammonium chloride, and 0-0.5 mols (SiO_2) of silicon dioxides of cylindrical meso porous fine particles are dissolved in 1l. ion exchange water. Then, cylindrical meso porous fine particles were obtained like said example 10. In addition, it was referred to as $2 < 1.3$ mols of $\text{Na}_2\text{SiO}_3+\text{SiO}_2(\text{s})$. Within the limits of this, each was able to prepare cylindrical meso porous fine particles.

[0061] Example 15 0.5-1.2 mols (Na_2SiO_3) of manufacture specific metasilicate, 0.05-0.24 mols (STB) of stearyl trimethylammonium star's pictures, and 0.2-2 mols (NaBr) of sodium bromides of cylindrical meso porous fine particles are dissolved in 1l. ion exchange water. Henceforth, cylindrical meso porous fine particles were obtained like said example 10. In addition, it was referred to as $\text{Na}_2\text{SiO}_3/\text{STB}/\text{NaBr}=1/0.1/1-4$ thru/or $1/0.2/1-2$. Within the limits of this, each was able to prepare cylindrical meso porous fine particles.

[0062] Moreover, if the cylindrical meso porous fine particles manufactured according to this invention have high oil absorption nature, for example, it blends with skin external preparations, such as cosmetics, extremely as mentioned above, they can adsorb sebum suitably and can raise the holding power on the skin. Thus, the loadings in the case of blending perfume maintenance fine particles into skin external preparations are arbitrary according to the gestalt of cosmetics, and, generally are 0.1 - 80 % of the weight. In the case of the product of emulsification and a dispersed system, 0.1 - 10 % of the weight is common, and powdered or when it is the product of powder pressed **, 0.1 - 70 % of the weight is common.

[0063] Moreover, in addition to the above-mentioned perfume maintenance fine particles, the component of others which are generally blended to external preparations can be blended in the qualitative and quantitative range which does not spoil the effectiveness of this invention. For example, a moisturizer, a wax, a pigment, an oil content, a surfactant, antiseptics, an antioxidant, a chelating agent, alkali, a water soluble polymer, an oil solubility macromolecule, a clay mineral, etc. can be mentioned. Hereafter, the example of concrete combination of the cosmetics which blended the perfume maintenance fine particles as an example of this invention is explained.

[0064]

Example 1 of combination Lip stick Polyethylene wax 3% Ceresin wax 10 Coll navarho 2 Candelilla low 5 Liquid paraffin 30 Castor oil 15 G 2-heptyl undecanoic acid glycerol 20 Olive oil 11 Red iron oxide 0.2 Red No. 202 1.8 Perfume maintenance fine particles The heating dissolution of 2 <process> oil contents and the wax is carried out at 85-90 degrees C, and a pigment is added to this thing and it distributes. Reduced pressure deaeration was carried out promptly, it moved to the predetermined container, cooling solidification was carried out, and the lip stick was obtained. This lip stick was what cannot fall easily after spreading.

[0065]

Example 2 of combination Press-like eye shadow Talc 26 Mica 35 Titanium-coated mica 20 Liquid paraffin 2.8 Dimethylpolysiloxane (6cs) 2 Perfume maintenance fine particles 5 Sorbitan mono-olate 1 Ultramarine blue 8 Red No. 201 After mixing the powder except 0.2 <process> titanium-coated mica with a Henschel mixer, the oil content and the surface active agent were added and the pulverizer ground. Furthermore titanium-coated mica was added and it mixed to homogeneity with the Henschel mixer. Compression molding of this thing was carried out at the predetermined inside pan, and eye shadow was obtained.

[0066]

Example 3 of combination Powder Perfume maintenance fine particles 40 Talc 58.7 Citric acid 0.2 Red ochre 0.01 Liquid paraffin 1 Perfume 0.09 <process> citric acids are dissolved in alcohol 99%, and it adds to talc, and a Henschel mixer removes the mixing back and alcohol is removed at 80 degrees C. Furthermore the remainder is added and an atomizer grinds. Moving powder is obtained as it is in a predetermined container.

[0067]

Example 4 of combination Emulsification foundation Stearin acid 0.7 Isopropyl myristate 4 Squalane 22 Polyoxyethylene (ten mols) stearyl ether 2 Cetyl alcohol 0.3 Talc 7 Perfume maintenance fine particles 3 Iron oxide pigment 2.5 Red No. 202 0.5 Antiseptics 0.09 Triethanolamine 0.42 Propylene glycol 5 Purified water 52.19 Perfume After carrying out the heating mixing dissolution of 0.3 <process> oil contents and the surfactant, the pigment section is added and it distributes to homogeneity. What dissolved and heated triethanolamine and propylene glycol in purified water to this is added and emulsified. Churning cooling of this was carried out, and perfume was added, it was made homogeneity, the container was filled up, and emulsification foundation was obtained.

[0068]

Example 5 of combination Rouge Talc 30 Mica 35 Titanium oxide 3 Titanium-coated mica 5.5 Red No. 202 0.5 Perfume maintenance fine particles 3 Sorbitan diisostearate 1 Squalane 7 Methylphenyl polysiloxane 15 <process> pigment section is mixed, and to this, the heating dissolution is carried out, and other components are added, and are mixed and ground to it. This was cast to the inside pan and press-like rouge was obtained.

[0069]

Example 6 of combination Liquefied eyeliner Isoparaffin 58.97 Hydrocarbon system resin 5 Cull navarro 1 Candelilla low 5 Cholesterol 2 Ethyl alcohol 5 Purified water 8 Organic denaturation montmorillonite 3 Iron black 10 Perfume maintenance fine particles 1 Sorbitan monostearate 1 An activator, water, an organic denaturation montmorillonite, and a pigment are added to a part of perfume 0.03 <process> isoparaffin, and distributed mixing is carried out at homogeneity and it is made 85 degrees C. The remainder of isoparaffin, resin, and a wax are added to an iron pot, and it is made to dissolve in homogeneity at 90 degrees C. The dispersion liquid prepared beforehand here are added and distributed mixing is carried out at 85 degrees C -- 90 degrees C, and perfume is added and annealed and it may be 30 degrees C. A predetermined container is filled up and a waterproof eyeliner is obtained.

[0070]

Example 7 of combination Foundation in two ways Siliconization titanium oxide 20 Siliconization mica 22 Siliconization iron oxide 3 Perfume maintenance fine particles 5 Liquid paraffin 4.5 Methyopolysiloxane (100cs) 25 Methyl hydrogen polysiloxane (20cs) 20 Sorbitansesquiolate An oil content and an activator are added after mixing the 0.5 <process> pigment section to homogeneity, and it mixes. Press molding is carried out after grinding with an atomizer at a predetermined inside pan. As explained above, its holdout on the skin is good while the skin external preparations which blended perfume maintenance fine particles are excellent in the maintenance effectiveness of perfume, and, moreover, a feeling of an activity can be made good.

[0071]

[Effect of the Invention] According to the perfume maintenance fine particles which start this invention as explained above, and its constituent, it is homogeneous, and since perfume was made to hold to the meso porous fine particles which moreover have the meso hole of the diameter of detailed and which use oxidation silicon as a principal component, stripping of stable maintenance and constant speed can be planned over a long period of time [the].

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view of the perfume maintenance effectiveness by the perfume maintenance fine particles concerning this invention.

[Drawing 2] It is the explanatory view showing silicate concentration (0.15M) and the relation of a crystallized state.

[Drawing 3] It is the explanatory view showing silicate concentration (0.5M) and the relation of a crystallized state.

[Drawing 4] It is the explanatory view showing silicate concentration (1.0M) and the relation of a crystallized state.

[Drawing 5] It is the explanatory view showing silicate concentration (1.5M) and the relation of a crystallized state.

[Drawing 6] It is the explanatory view showing the acid addition rate for pH adjustment (2 ml/min), and the relation of a crystallized state.

[Drawing 7] It is the explanatory view showing the concentration (0.2Ns) of the acid for pH adjustment, and the relation of a crystallized state.

[Drawing 8] It is the explanatory view showing the concentration (5.0Ns) of the acid for pH adjustment, and the relation of a crystallized state.

[Drawing 9] It is the TEM photograph in which the structure of the massive meso porous fine particles obtained by this invention is shown.

[Drawing 10] It is X diffraction drawing of the massive meso porous fine particles obtained by this invention.

[Drawing 11] It is nitrogen adsorption isotherm drawing of the meso porous fine particles shown in drawing 10 .

[Drawing 12] It is the explanatory view of the diameter distribution of opening of the meso porous fine particles shown in drawing 10 .

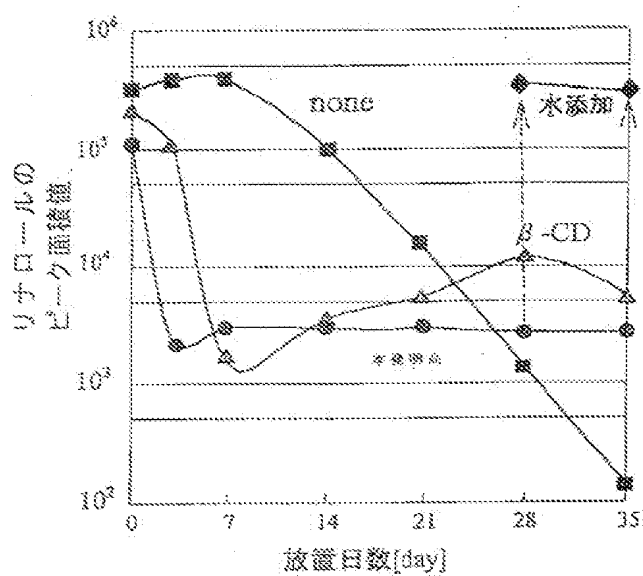
[Drawing 13] It is X-ray diagram *** of the massive meso porous fine particles obtained by this invention.

[Drawing 14] It is X-ray diagram *** of the cylindrical meso porous fine particles obtained by this invention.

[Drawing 15] It is nitrogen adsorption isotherm drawing of the meso porous fine particles shown in drawing 14 .

[Drawing 16] It is the explanatory view of the diameter distribution of opening of the meso porous fine particles shown in drawing 14 .

[Translation done.]



[Translation done.]

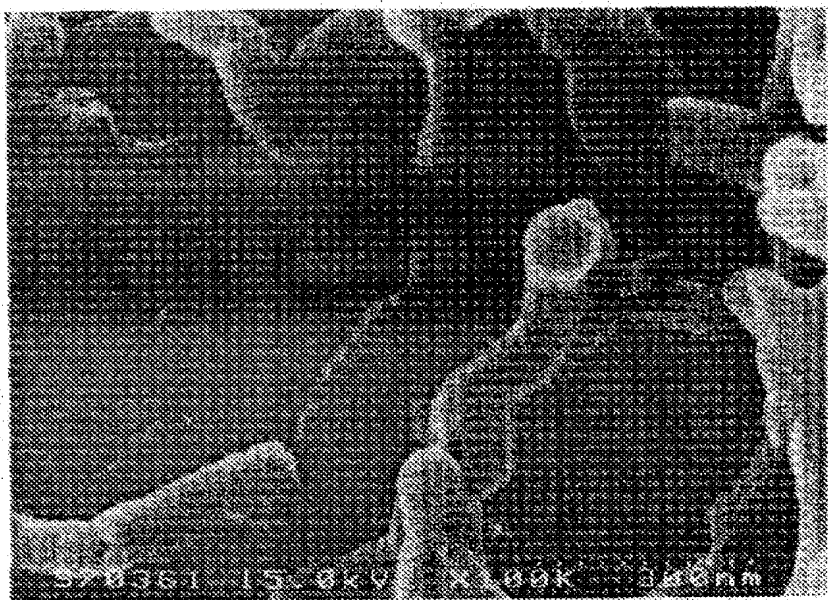
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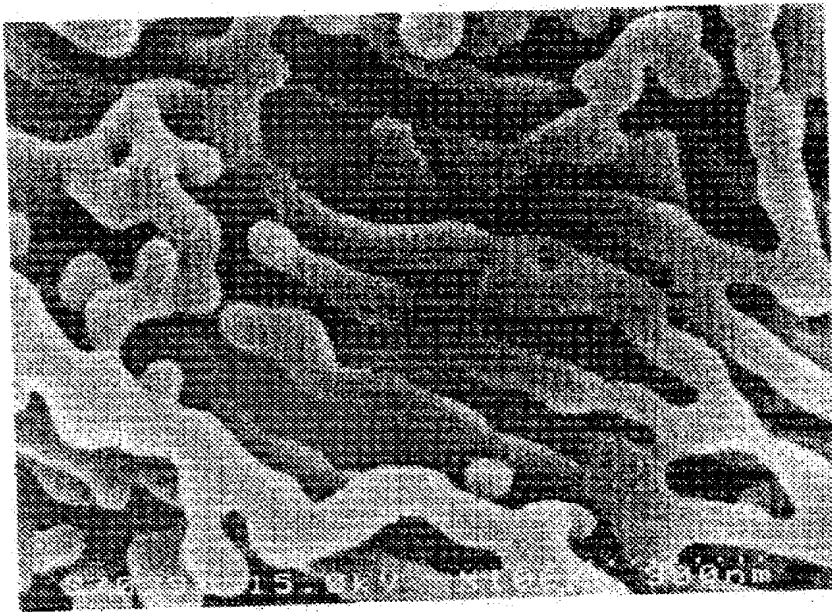
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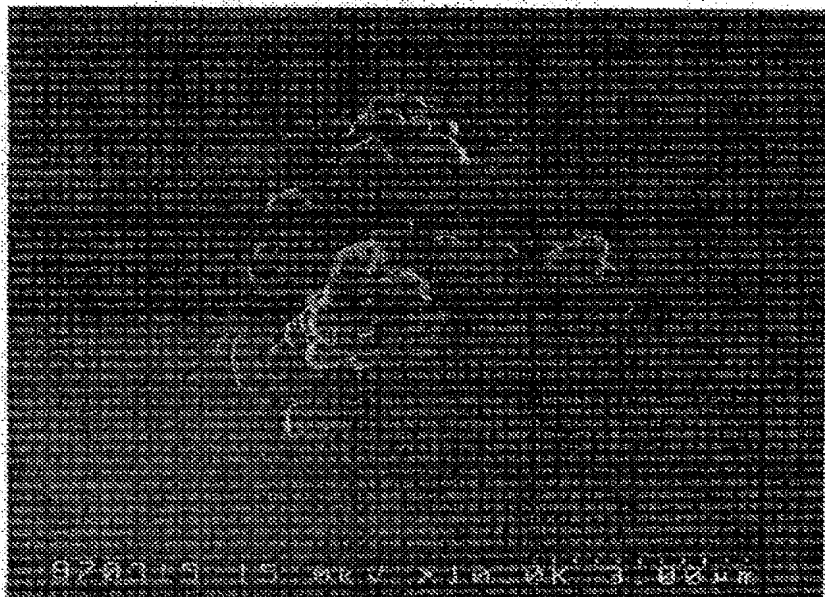
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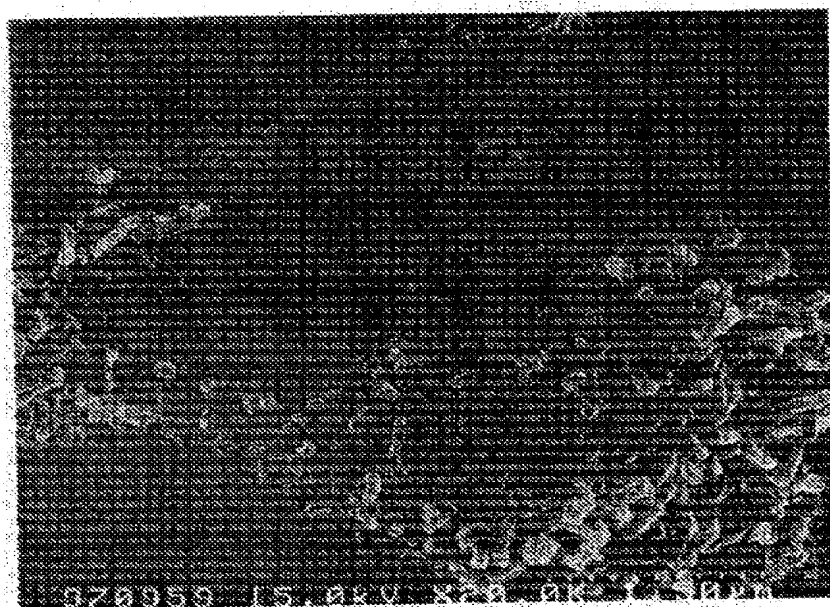
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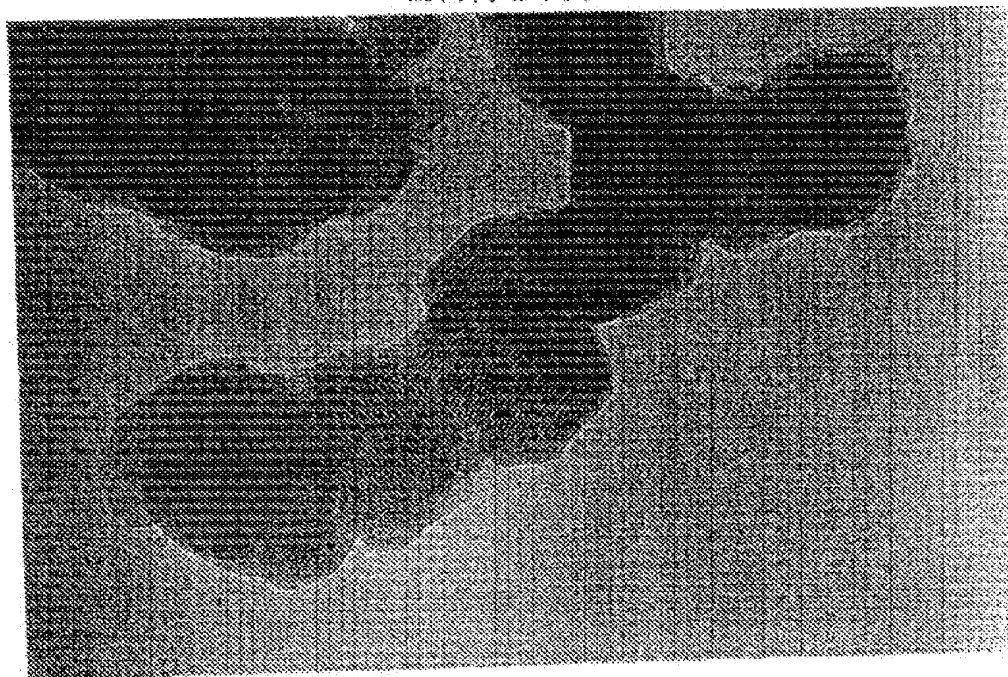
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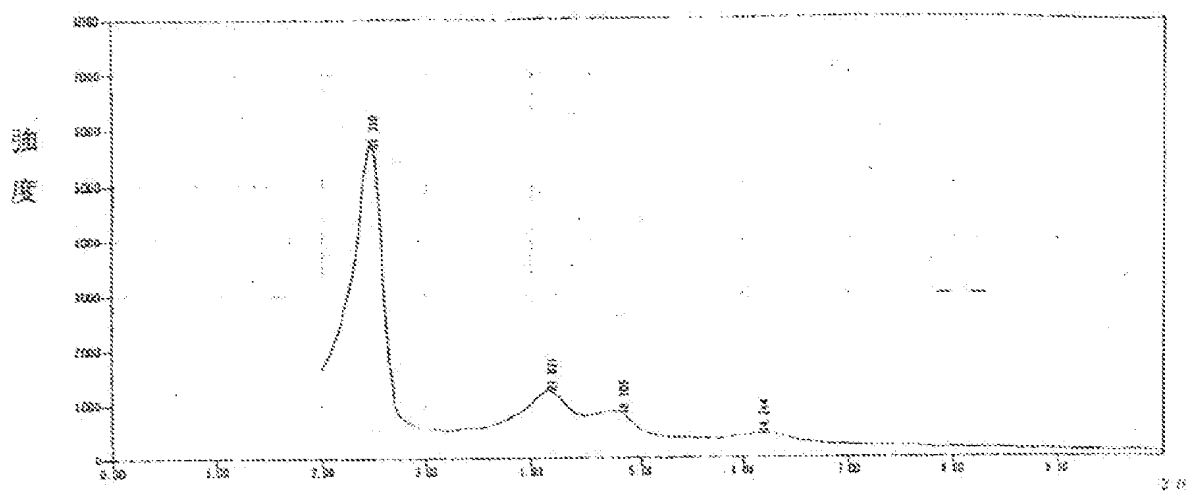
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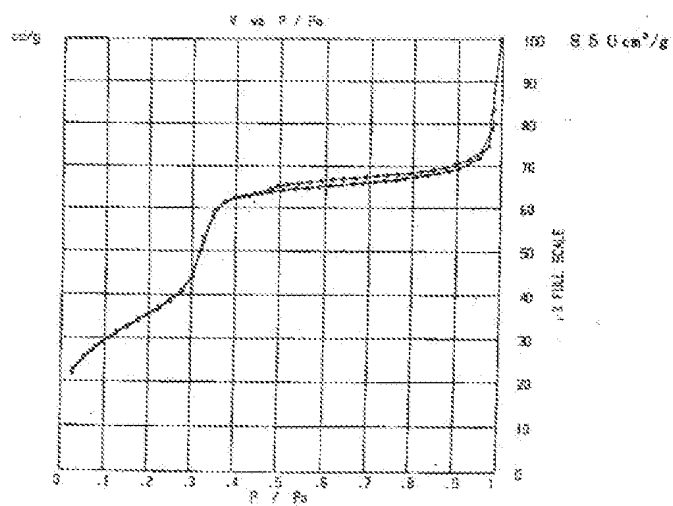


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Drawing selection drawing 10

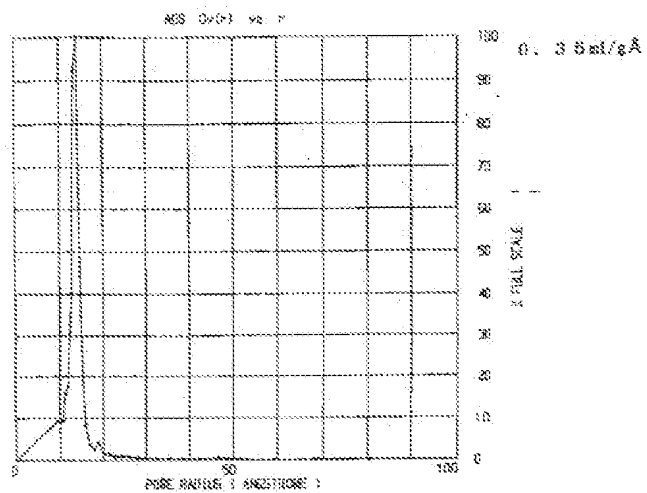


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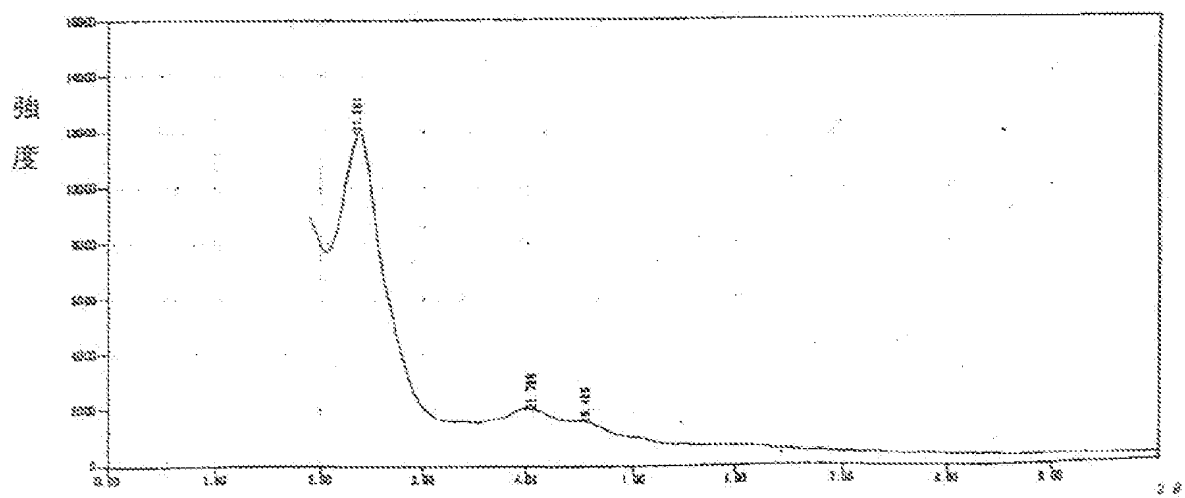
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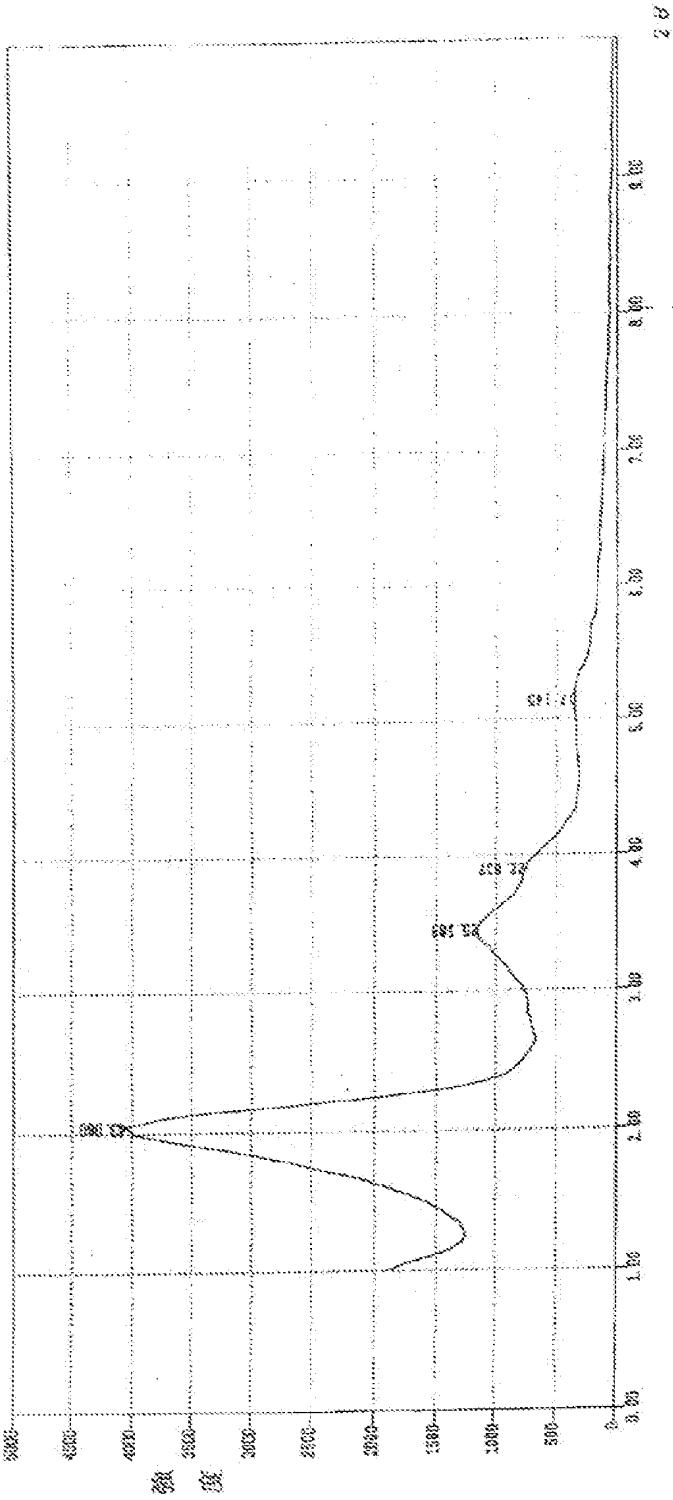


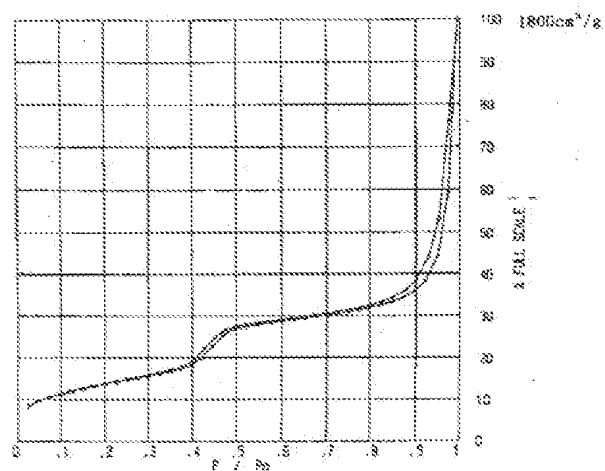
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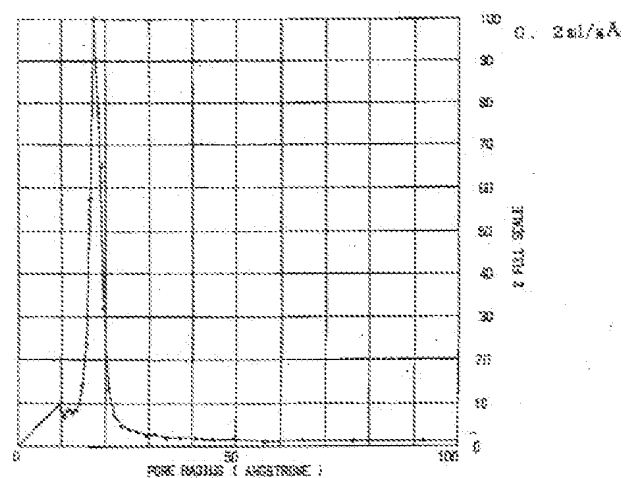
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